

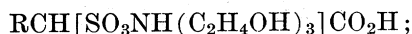
Detergent Bars from Salts of α -Sulfonated Tallow Acids^{1,2}

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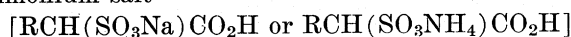
A SYNTHETIC DETERGENT BAR is expected to equal or approximate the excellent characteristics of soap in soft or moderately hard water, to be more efficient than soap in very hard water, and perhaps to be useful in sea water as well. Detergent bars are judged with reference to soap as a standard. From consideration of the many problems encountered in the development of detergent bars (7, 8, 9, 10), such tallow derivatives as α -sulfonated tallow acids, $\text{RCH}(\text{SO}_3\text{H})\text{CO}_2\text{H}$, or their salts should be quite suitable because of the resemblance to soap in chemical and physical properties.

Acid $[\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{H}]$, neutral $[\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{M}]$, or mixed salts $[\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{M}']$ can be made by selective neutralization of the strongly acid sulfonic or the weakly acid carboxyl group. Further sodium, ammonium, and substituted ammonium salts have been found to differ considerably in solubility and surface-active properties (15). Thus mixed salt compositions could be useful in synthetic detergent bars where controlled solubility is required. Accordingly the present report concerns experimental synthetic detergent bars which are 100% active, based entirely on selected salts of α -sulfonated tallow acids.

Satisfactory synthetic detergent bars could not be made from either the sodium or potassium salts alone, because of their limited solubility and decidedly crystalline character. Acid ammonium salts $[\text{RCH}(\text{SO}_3\text{NH}_4)\text{CO}_2\text{H}]$ gave hard brittle bars with poor solubility and lather, and bars from acid triethanolammonium salts were too soft and too readily soluble. However detergent bars useful in hard or sea water, with generally attractive cleaning and lathering properties, were made from salt combinations of the following types: A, a major amount of the disodium salt, $\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na}$, with a lesser amount of an acid triethanolammonium salt,



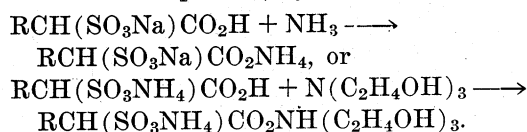
B, a major amount of the monosodium or monoammonium salt



with a lesser amount of an acid substituted-ammonium salt



C, a major amount of the monosodium or monoammonium salt with the carboxyl group partially neutralized by the addition of lesser amounts of ammonia or amines, or the addition of ammonia and amines. In this type mixed salt formation is presumed, in the bar formation process, by reactions such as



Preparation of Salts

α -Sulfonation. The reaction of liquid sulfur trioxide with purified stearic acid, or with distilled hydrogenated tallow acids⁴ with carbon tetrachloride as the solvent was carried out as described in previous publications (14). In some experiments commercial α -sulfopalmitic and α -sulfostearic acids⁵ were mixed in a ratio corresponding to hydrogenated tallow acids.

Sodium Salts. A concentrated aqueous sodium chloride solution was added in slight excess to a hot 10% aqueous solution of the α -sulfonated acid. The crystallized monosodium salt was extracted with warm acetone to remove unsulfonated fatty acid normally present to the extent of 0.2–1.0%. Crystallization from boiling water gave an 85–90% yield of the purified monosodium salt.

Disodium salts were prepared by neutralization of the monosodium salt prior to the final crystallization.

Ammonium Salts. Monammonium salts could be prepared from aqueous solution in the same manner as the monosodium salts, but neutralization of an alcoholic solution of the α -sulfonated acid with concentrated aqueous ammonia was a more convenient laboratory method. After precipitation the monoammonium salt was decolorized and recrystallized from 80% ethanol.

Substituted Ammonium Salts. Acid triethanolammonium salts were prepared by adding a slight excess of triethanolamine to an alcoholic solution of the α -sulfonated acid and were purified by recrystallization from alcohol and chloroform (15). Ethylammonium α -sulfostearic acid and ethanolammonium α -sulfostearic acid, prepared in the same way, had the following analyses,⁶ respectively: calculated for $\text{C}_{20}\text{H}_{43}\text{NO}_5\text{S}$, 3.42% N, 7.83% S (found 3.35, 7.61); calculated for $\text{C}_{20}\text{H}_{43}\text{NO}_6\text{S}$, 3.29% N, 7.53% S (found 3.26, 7.23).

Mixed Salts. Sodium ammonium α -sulfostearate was prepared by adding a slight excess of aqueous ammonia to a hot aqueous solution of the monosodium salt. The recrystallized precipitate had the following analysis⁶: calculated for $\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{NH}_4$, 3.47% N, 5.70% Na, 7.95% S (found 3.42, 5.76, 8.32).

Some properties of ammonium and related salts are shown in Table I. The acid ammonium salts and the sodium ammonium salt are the least soluble, the acid ethylammonium and ethanolammonium salts have intermediate solubility, and the acid triethanolammonium salts are exceedingly soluble. The immediate foam height (11) was about 200 mm. in each case, but the acid ammonium and the sodium ammonium salts had the most stable foam.

The Krafft point is significant with respect to synthetic detergents as well as soap. It is the temperature, somewhat independent of concentration, at which there is a marked increase in solubility with concomitant changes in the nature of the solution.

¹ Presented in part at the fall meeting, American Oil Chemists' Society, Cincinnati, Sept. 30–Oct. 2, 1957.

² No. XI in a series "Synthetic Detergents from Animal Fats." For No. X see reference (5).

³ One of the Laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

⁴ Supplied by Wilson-Martin Division, Wilson and Company, Philadelphia, Pa.

⁵ Supplied by Armour Chemical Division, Armour and Company (2).

⁶ Microanalyses for N and S were performed by Miss Laverne Scroggins.

TABLE I
Properties of Ammonium and Alkylammonium Salts of
 α -Sulfonated Acids

	Solubility 30° (g./100 ml.)	Krafft point ^a 1% so- lution (°C.)	pH 30° 0.1% solution
Ammonium α -sulfopalmitic acid.....	0.2	42	4.0
Triethanolammonium α -sulfopalmitic acid...	>20	<0	4.0
Ammonium α -sulfostearic acid.....	0.05	59	4.4
Ethylammonium α -sulfostearic acid.....	3	29	4.4
Triethanolammonium α -sulfostearic acid.....	5	28	4.5
Sodium ammonium α -sulfostearate.....	>20	<0	4.4
	0.1	60	7.0

^a Temperature at which a turbid dispersion became clear on gradual heating.

The Krafft points of Table I were determined by the procedure recommended for soaps (6): a hot clear 1% solution was cooled to turbidity, and the homogeneous dispersion was gradually reheated until clarification occurred.

Detergent Bar Formation

The detergent bars were generally made on a laboratory scale by means of a two-roll mill and a hydraulic press, but use of a small-scale plodder and stamping machine showed that it was also possible to use conventional soap bar-forming equipment.

Mill and Press Experiments. A total of 60 g. of the detergent salt composition of Type A or B and 7 g. of water was stirred together manually and allowed to stand over-night. The procedure was the same for Type C detergents, with a total of 60 g. of the monosodium or monoammonium salt plus a less than equivalent amount of ammonia, amine, or ammonia and amine.

The following day the moist composition was mixed on a two-roll rubber compounding mill. The rolls were closed during milling to simulate the action of a multiroll mill used to process soap. At the end of this operation a homogeneous plastic sheet was cut from the rolls.

The milled material was pressed into experimental bars $2\frac{1}{2} \times 1\frac{1}{2} \times \frac{1}{4}$ in., with a mass of 18–20 g., a volume of 17.0–18.5 ml., and a density of 1.00–1.15, by means of a three-piece, sandwiched mold and a hydraulic press.

Plodder and Stamping Machine. Through the kindness of Leopold Safrin ⁷ three pounds of the detergent

composition A of Table II were mixed in a small-scale plodder, and the extruded strands were stamped into bars in a hand-stamping machine. The composition, a mixture of the disodium salt and the acid triethanolammonium salt, was found to behave a great deal like soap in the plodder but had a slight tendency to stick to the mold in the stamping machine.

This experiment demonstrated correlation between processes and showed that synthetic detergent compositions based on salts of α -sulfonated tallow acids were adaptable to operations in conventional soap bar-forming equipment.

Properties of Experimental Detergent Bars

The properties which make a detergent bar acceptable to the user are difficult to measure in the laboratory. Properties of the detergent bar in use, essentially the resemblance to soap or improvement over soap in lather, cleaning action, feel, dish life, and absence of any dryness or discomfort, may be rated differently, depending on the user's own habits and preference. Measurements of foam height and emulsification are probably helpful in initial screening but cannot correlate with subjective impressions of lather and cleaning action.

Hardness and Solubility. Hardness and solubility are significant properties which can be measured and are related to observations in both the bar-forming process and the hand-washing tests.

Hardness was measured with a Shore Durometer,⁸ Type A, following a procedure used to estimate the approximate hardness of rubber (1). The immediate gauge reading is recorded in Table II.

Comparative solubility was conveniently measured by use of the Deter-Meter⁸ (16) in a manner somewhat similar to the use of other instruments to measure shampoo performance (3) and lather quickness (4). The experimental detergent bar, placed in the cage of the Deter-Meter,⁸ with screens set at minimum clearance, and medium stroke length (2 in.), plunged repeatedly (100 strokes, 60 cycles per minute) into 3,500 ml. of laboratory tap water (80 p.p.m.) at 110°F. Relative rate of foam generation can be observed in this process. The detergent bar was air-dried over-night, and weight loss was recorded as a measure of solubility.

⁸ Reference to a manufactured instrument does not imply recommendation by the U. S. Department of Agriculture over similar instruments not mentioned.

TABLE II
Effect of Composition on the Properties of Detergent Bars

Type	Detergent bar composition, mole %, dry basis as salts of α -sulfonated hydrogenated tallow acids	Water (% by wt.)	Hardness ^a	Weight loss, g., in solubility test ^b	Lather in handwashing test	Comparative dish life, appearance of wetted surface
A.....	80-RCH(SO ₃ Na)CO ₂ Na 20-RCH[SO ₃ NH(C ₂ H ₄ OH)] ₃ CO ₂ H	1.7	50	4.7	flash lather	chalky
B.....	80-RCH(SO ₃ NH ₄)CO ₂ H 20-RCH[SO ₃ NH(C ₂ H ₄ OH)] ₃ CO ₂ H	1.6	65	5.9	somewhat thin flash lather	chalky
C-1.....	60-RCH(SO ₃ Na)CO ₂ H 40-RCH(SO ₃ Na)CO ₂ NH ₄	1.6	100	0.07	slow forming thick lather	no change
C-2.....	70-RCH(SO ₃ Na)CO ₂ H 30-RCH(SO ₃ Na)CO ₂ NH ₃ C ₂ H ₄ OH	0.5	98	1.1	flash lather	no change
C-3.....	80-RCH(SO ₃ Na)CO ₂ H 20-RCH(SO ₃ Na)CO ₂ NH(C ₂ H ₄ OH) ₃	3.5	59	3.6	flash lather	thin chalky layer
C-4.....	72-RCH(SO ₃ Na)CO ₂ H 8-RCH(SO ₃ Na)CO ₂ NH(C ₂ H ₄ OH) ₃ 20-RCH(SO ₃ Na)CO ₂ NH ₄	4.8	70	1.0	thick copious lather	very thin chalky-layer
C-5.....	85-RCH(SO ₃ NH ₄)CO ₂ H 15-RCH(SO ₃ NH ₄)CO ₂ NH ₃ C ₂ H ₄ OH	3.2	72	3.8	thick copious lather	slightly gelatinous
C-6.....	50-RCH(SO ₃ Na)CO ₂ NH ₄ 30-RCH(SO ₃ Na)CO ₂ NH(C ₂ H ₄ OH) ₃ 20-RCH(SO ₃ Na)CO ₂ H	4.4	45	4.3	copious lather	chalky

^a Immediate reading with Shore Durometer⁸ (1). ^b Measured in the Deter-Meter⁸ (16) at 110°F.

Dish Life. The comparative "dish life" or "sloughing" tendency was estimated in a test similar to that described by Toof (13). The detergent bar was supported in $\frac{1}{8}$ in. of hard water (300 p.p.m.), resting on two $\frac{1}{16}$ -in. bent stainless steel rods. After 10 min. of contact the appearance of the wetted under-surface was an indication of the behavior to be expected in use, when the wet detergent bar rests in the soap dish.

Water Content. Although the detergent bar compositions were prepared with an initial water content of about 12%, it was found that much of this was lost in bar formation, particularly in the milling operation. The amount of water in the detergent bar can be regulated somewhat by the length of time in the milling operation but was usually less than 5%. A greater water content decreases hardness and increases solubility.

Irritant Tests. Guinea pig skin and rabbit skin and eye tests for irritation and sensitization were carried out by Floyd DeEds and associates⁹ on the detergent bars A, C-1, and C-2 of Table II and the salts from which they were formed. Detergent A produced a minor degree of irritation in the guinea pig skin test, which however was not greater than that caused by a commercial hand soap. No sensitization occurred, and rabbit skin and eye tests were negative.

The results of the animal tests appear encouraging but are preliminary, and clinical tests would eventually be required.

Discussion

The data of Table II list the properties of representative detergent bars of types A, B, and C. Combination of the neutral sodium salt and an acid substituted-ammonium salt (A) gave a good detergent bar, somewhat too soft and readily soluble except in very hard water or sea water. Combination of two kinds of acid salts (B) gave detergent bars characterized by a rather thin and nonpersistent lather.

For convenience and from practical considerations most of our experiments concerned type C compositions, based on the readily available monosodium salt, to which it was only necessary to add varying amounts of ammonia or amines. A purified monosodium salt was used, but it may also be possible to use a monosodium salt formed directly from the sulfonation reaction without isolation of the α -sulfonated acid.

The hardness, solubility, lather characteristics, and dish life correlate in a general way. A hardness value of about 60 to 80 and a weight loss of from 1 to 4 g. indicate the best performance. Toilet soaps and present commercial detergent bars have values in this range. The "flash" lather is a readily formed attractive lather with larger bubbles than is usual for soap. The "thick copious" lather is readily formed and more persistent, with smaller bubbles (Figure 1).

The properties conferred by salt formation with ammonia, ethylamine, ethanolamine, or triethanolamine are indicated in Table I and shown more explicitly in Table II. Partial neutralization with ammonia (C-1) gave a hard shiny brittle bar with poor milling and molding properties and with a thick lather in spite of limited solubility. Neutrali-

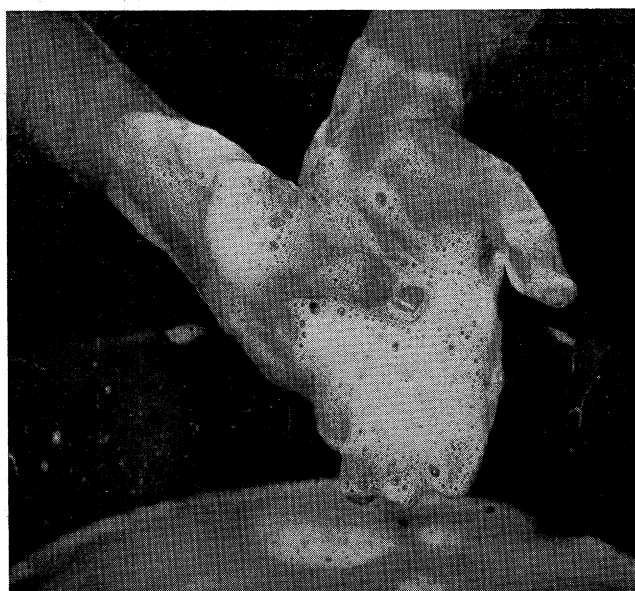
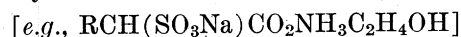


FIG. 1. Thick copious lather characteristic of detergent bar composition C-5, Table II.

zation with triethanolamine (C-3), isopropanolamine, or triethylamine tends to produce a soft, easily soluble bar. Neutralization with ethanolamine (C-2) or ethylamine tends to give quite satisfactory bars with intermediate properties. The best detergent bars of Table II, for soft and hard water, are believed to be C-4 and C-5.

Partial rather than complete neutralization of the carboxyl group is considered to result in some economy, greater plasticity, and an acid pH near that of the human skin. In some cases a detergent bar composed only of the neutral mixed salt



has desirable properties.

Soap-Syndet Combinations. The detergent bar compositions are compatible with soap, sodium stearate, or stearic acid, in the bar-forming process. Such mixtures have not been very closely investigated, and an opportunity exists to discover particularly favorable combinations.

Use in Sea Water. Some of the softer and more soluble bars were useful in sea water. Compositions A and C-6 gave thick attractive lathers in sea-water hand-washing tests. These detergent bars were more soluble in synthetic sea water (13) than were the other compositions of Table II. Neutralization of the acid sodium or acid ammonium salt with 50 mole per cent triethanolamine also gave bars which performed well in sea water but were somewhat soft for good milling or molding characteristics.

Summary and Conclusions

Experimental detergent bars were based entirely on selected salts of α -sulfonated saturated tallow acids. Some compositions appear to merit further investigation for the production of finished detergent bars, and an opportunity exists for the discovery of favorable combinations with soap. General conclusions are these.

1. Attractive detergent bars can be made from the monosodium or monoammonium salt $[RCH(SO_3M)CO_2H]$ by partial

⁹ Pharmacology Section, Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif.

neutralization with an amine or mixture of amines. Representative bars had the following compositions in mole percentage, anhydrous basis: a) 72 monosodium, 20 sodium ammonium, 8 sodium triethanolammonium salts; b) 85 monoammonium, 15 ammonium ethanolammonium salts.

2. Hardness and solubility can be controlled by water content and particularly by choice of the amine and the extent of the partial neutralization. Triethanolamine, isopropanolamine, and triethylamine tend to produce softer and more soluble bars than do ethanolamine or ethylamine.

3. The following compositions were suitable for detergent bars useful in sea water: a) 80 mole percentage of disodium 20 acid triethanolammonium; b) 20 monosodium, 50 sodium ammonium, 30 sodium triethanolammonium.

Acknowledgment

We are pleased to acknowledge the advice and assistance of Leopold Safrin, through whom it was possible to form detergent bars in a plodder and stamping machine. We are indebted also to Floyd DeEds and associates for the pharmacological tests on the detergent bars and the component salts. This considerable assistance is gratefully acknowledged.

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